552-76

INTERFACE MORPHOLOGY DURING CRYSTAL GROWTH: EFFECTS OF ANISOTROPY AND FLUID FLOW

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ABSTRACT

The effect of a parallel shear flow and anisotropic interface kinetics on the onset of instability during growth from a supersaturated solution is analyzed. The model used for anisotropy is based on the microscopic picture of step motion. A shear flow (linear Couette flow or asymptotic suction profile) parallel to the crystal-solution interface in the same direction as the step motion decreases interface stability. A shear flow counter to the step motion enhances stability and for sufficiently large shear rates the interface is absolutely morphologically stable. For large wave numbers, the perturbed flow field can be neglected and a simple analytic approximation for the stability-instability demarcation is found.

INTRODUCTION

During crystal growth or solidification of a binary alloy from a liquid phase, temperature and solute gradients are inherently present. In a gravitational field, these gradients can give rise to fluid flow in the melt. The interaction of fluid flow with the crystal-melt interface [1, 2] plays an important role in determining the properties of the solidified material. Convection in the melt and interface instability may both produce solute inhomogeneities. In the absence of fluid flow, the conditions for the onset of morphological instability are well established. However, the coupling between morphological instability and fluid flow can be complicated; interfacial instabilities depend on temperature and solute gradients which may be strongly influenced by the flow field. The flow field, in turn, may be influenced by the morphology of the interface.

Previously, we have carried out a number of theoretical investigations relevant to the experimental studies in space by J. J. Favier and colleagues (Centre d'Etudes Nucleaires de Grenoble) and R. Abbaschian and colleagues (University of Florida) utilizing the MEPHISTO apparatus [3]. In the MEPHISTO space experiments, dilute alloys of tin containing bismuth (USMP-1 & 3) and bismuth containing 0.1 at.% tin (USMP-2) were directionally solidified for growth conditions in the vicinity of the planar-cellular transition. While tin is fairly isotropic, bismuth is extremely anisotropic forming facets during growth. We first discuss recent results on the morphological stability of highly anisotropic materials.

During alloy solidification, a smooth crystal-fluid interface may become unstable, leading to cellular or dendritic growth. Linear morphological stability theory [4, 5] describes the conditions under which the interface becomes unstable. The original treatment of morphological stability by Mullins and Sekerka assumed local equilibrium at the crystal-melt interface and isotropy of the crystal-melt surface tension; this is an excellent approximation for many metals at low growth velocities. However, many materials, including semiconductors and metals such as gallium and bismuth, grow with facets indicating strong anisotropy and deviations from local equilibrium. The stability of faceted growth has also been reviewed [6]. The effect of anisotropy of surface tension and interface kinetics on morphological stability has been treated in a quasi-static approximation to the diffusion field; kinetic anisotropy causes traveling waves along the crystal-melt

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interface [7]. Yuferev [8] showed that for growth in which the interface is near a singular orientation (an atomically smooth orientation), there is an enhancement of morphological stability; more detailed calculations for a binary alloy [9] and for growth into a supersaturated solution [10] and supercooled melt [11] have been carried out. Recently, we have considered the effect of shear flows and anisotropic interface kinetics on the morphological stability of a binary alloy growing from the melt [12].

The motion of elementary steps is the essence of layerwise growth and decrystallization (dissolution, melting, or evaporation). Step motion has the well-known tendency for not always proceeding as regular step trains, i.e., keeping the interstep distance constant and producing homogeneous crystals. Instead, under a wide range of conditions, the elementary steps cluster into step bunches. In other words, the interface is morphologically unstable with respect to step bunching. The step bunches trap impurities in amounts which depend on the local step densities, and therefore the impurity distribution differs from that formed by regular step trains. As a result, bands enriched or depleted in point-defects appear in the grown crystal [13]. Step bunches themselves may, in turn, lose their stability and trap inclusions of solvent. Growth conditions under which these instabilities are less likely typically require experimental determination; they are not well understood quantitatively and in some cases not even qualitatively. It is well known, however, that fluid flow in the solution, crystal growth rate, and impurities are of great importance for the onset of step bunching. This is the motivation for analyzing the effect of flow on step bunching, i.e., on the morphological stability of vicinal faces in solution and melt growth. If the role of flow effects is understood, the influence of other factors on crystal quality may be better discerned.

Experiments and theory indicate that a solution flowing above a vicinal face of a crystal can either enhance or prevent the development of step bunches [6, 14, 15, 16]. In the absence of flow, anisotropic kinetics arising from the motion of steps on the crystal surface provides an important self-stabilization mechanism [8, 9, 10, 11].

In this manuscript, we treat the effect of shear flows on the morphological stability of a crystal growing from solution by a step mechanism at a given constant velocity $\bar{V}$. In the absence of flow the self-stabilization due to anisotropic kinetics has been treated [10] and we employ the same model here. The effect of flow on morphological stability of stepped surfaces has been treated previously ignoring the perturbed flow field [15]. We will explore this approximation and show that it is valid for a range of growth conditions.

THEORY

In order to phenomenologically treat anisotropic kinetics, we assume that growth is by the motion of elementary steps, which leads to a macroscopic anisotropic kinetic law. The interface kinetic coefficient $\beta(p)$, defined as the ratio of the solute flux and the deviation $(C_I - \bar{C}_e)$ of the interface concentration C_I from the equilibrium solution concentration $\bar{C}_e$, is given by $\beta(p) = \beta_{st}|p|$, $p = \tan\theta$, where θ measures the deviation of the slope of the interface from a singular orientation [6]. If the planar interface is a singular interface ($p = 0$), its kinetic coefficient vanishes and in this model there is no growth. In reality, a singular interface becomes macroscopically or locally vicinal due to a screw dislocation or a two-dimensional nucleation mechanism, which generates steps. A locally finite value of p at any macroscopic area of the interface results. The unidirectional step motion introduces anisotropy and we will only consider perturbations along the direction of the step motion. Further, we assume that the perturbations are sufficiently small that the quantity p does not change sign.

Our sign convention is such that positive p corresponds to step motion to the left (negative x direction, see Figure 1a). If we consider a small sinusoidal perturbation of a planar interface characterized by a constant positive value of $p = \bar{p}$, then regions of the perturbed interface with positive slopes will have larger values of p and therefore larger kinetic coefficients and larger step densities. Thus for the same supersaturation, regions of the interface with positive slopes will grow faster than regions with negative slope; this leads to a translation of the sinusoidal perturbed interface in the direction of the step motion.

As previously discussed [9, 10, 15, 16], both this lateral translation of the sinusoidal interface perturbation and the lateral flow of liquid can move a depression in the interface to a solute-enriched region of solution where it can grow faster and thus provide a stabilizing mechanism.

A shear flow in the opposite direction from the step motion tends to move fluid into the steps and is somewhat equivalent to a faster translation of the perturbations in a stagnant fluid; therefore, one expects such a flow to further stabilize the interface. Conversely, a shear flow in the direction of the step motion will destabilize the interface. Thus, the key physics behind the stabilization or destabilization is the phase shift between the perturbation of the interface shape (characterized by alternation of higher and lower step density running tangentially along the interface) and the concentration waves induced by these step bunches (also traveling parallel to the interface). This phase shift is influenced by both the motion of the step bunches and the solution flow.

We have carried out a linear stability analysis for constant velocity growth in the $z-$direction into a supersaturated solution. We solve the incompressible Navier-Stokes equations for the fluid velocity $\boldsymbol{u}$ and the convection-diffusion equation for solute concentration $C(x, z, t)$ in the absence of gravity. We consider a two-dimensional problem and assume all quantities are independent of the coordinate y. The basic equations and boundary conditions are given in references [10] and [12].

For the linear stability analysis of the base state, the variables are written as the superposition of the base state component and a perturbation. The perturbed quantities are Fourier analyzed in the lateral direction and exponential time-dependence is assumed, so that the perturbed variables are proportional to $\exp(\sigma t + ik_x x)$ where $\sigma = \sigma_r + i\sigma_i$ is the complex temporal growth rate, and k_x is the wavenumber in the x-direction. The numerical solution procedures used to solve the resultant differential eigenvalue problem have been described previously [12].

RESULTS and DISCUSSION

We have carried out a series of calculations using the following parameters: diffusion coefficient $D = 1.0 \times 10^{-5}\,\mathrm{cm}^2/\mathrm{s}$, capillary parameter $\Gamma = 5.0 \times 10^{-8}\,\mathrm{cm}$, $C_s/\bar{C}_e = 5$, $\beta_{st} = 0.1\,\mathrm{cm/s}$, $\nu = 0.01\,\mathrm{cm}^2/\mathrm{s}$, and $\rho = 1$ [15], where C_s is the concentration in the crystal, ν is the kinematic viscosity, and $\rho = \rho_S/\rho_L$ is the ratio of the crystal and solution densities ρ_S and ρ_L. Numerical calculations were carried out for unperturbed flows corresponding to both linear Couette flow (in which the flow velocity increases linearly with distance from the interface and the shear rate is independent of distance) and the asymptotic suction profile (in which the flow velocity attains a constant value far from the interface and the shear rate decays exponentially). However, for a given shear rate S at the interface, the results for both profiles are essentially identical.

In Figure 2 for $\bar{p} = 0.01$, we plot (solid curves) the wavenumber k_x as a function of growth velocity $\bar{V}$ for $\sigma_r = 0$ for various shear rates. The result for zero shear is the same as previously given [10], with the system being stable for large velocities and large wavenumbers. Stability at large wavenumbers is a result of capillarity while anisotropic kinetics provides stability at intermediate wavenumbers. Negative shear (flow in the direction of the step motion) destabilizes the interface, particularly at small wavenumbers. The curve for $S = -0.1\ \mathrm{s}^{-1}$ has a minimum at small wavenumbers and large velocities. Below this minimum wavenumber the system is unstable for all velocities. Above this minimum wavenumber there is a region of stability at intermediate velocities. Positive shear (flow opposite to the direction of the step motion) stabilizes the interface. At a shear rate of $0.1\ \mathrm{s}^{-1}$, the neutral curve forms a closed loop with instability occurring inside the loop. Above a shear rate of $0.629\ \mathrm{s}^{-1}$, we have not found any modes with $\sigma_r \geq 0$ indicating that the system is stable for shear rates greater than this value. Following Chernov [15], we have also solved the stability problem by neglecting the perturbed flow. The results for the same conditions are given by the dashed curves in Figure 2. The dashed curves are only visible for $S = -0.1\ \mathrm{s}^{-1}$ at low wavenumbers indicating that the perturbed flow field is unimportant at high wavenumbers.

Since it is a good approximation to neglect the perturbed flow field, the perturbed solute field can be obtained analytically in terms of Airy functions. For large wavenumbers, the Airy function can be simplified by using its asymptotic representation, and we can obtain a simplified stability criterion, namely

$$\left\{\frac{\sigma_i}{k_x}\right\}\left\{\frac{\sigma_i}{k_x}+\frac{S}{2k_x}\right\} > 2Dk_x\bar{V}\left\{1-\frac{\bar{C}_e\Gamma Dk_x^2}{(C_s-\bar{C}_e)\rho\bar{V}}\right\}, \tag{1}$$

with

$$\sigma_i = \frac{\bar{V}\beta_{st}\zeta^2}{D(1+\zeta)}, \tag{2}$$

where $\zeta = Dk_x/(\beta_{st}\bar{p})$.

In the absence of capillarity, the above stability criterion can be written simply as

$$v_x + S/(2k_x) > 2\bar{p}(Dk_x + \beta_{st}\bar{p}), \tag{3}$$

where $v_x = \sigma_i/k_x$ is the magnitude of the phase velocity.

To better understand the physics behind the stabilization mechanism, we consider the concentration field above the perturbed interface within the general framework employed earlier [10, 15]. The perturbed stepped interface is shown in Figure 1a, where the numbers 1-3 are used to indicate specific regions of the perturbed stepped interface. The solution is evidently depleted with respect to the average solute concentration above regions of the type 1 where the step density (and thus ability of the interface to incorporate solute) is higher than the average step density (for an unperturbed interface). Conversely, the solution is enriched above the low step density areas (type 2). The perturbed solute distribution as a function of x and z is shown schematically in Figure 1b; the lowest wavy line is in the immediate vicinity of the interface.

The amplitude of the concentration waves at a distance z from the interface decreases as z increases. The typical decay length is $\approx k_x^{-1}$. The decay of the amplitude is depicted by the upper wavy lines in Figure 1b. These concentration waves would be stationary if neither the solution nor the interface pattern moved, as would be the case for a non-stepped, isotropic rough interface in a stagnant solution. Actually, both the step bunches and the solution move with respect to the crystal lattice. Therefore, each solution layer parallel to the interface moves tangentially with respect to the step pattern. Correspondingly, the phase shift of the concentration wave in each layer increases with z. In Figure 1b, each neighboring concentration wave is shown shifted to the right, following the solution flow relative to the step bunches.

The flow-induced morphological stabilization or destabilization results from the influence of the solution flow on the phase shift between the concentration waves and the perturbed interface waves. The shift of the surface concentration maxima, say, points A and B in Figure 1b, to the right causes stabilization because enriched solution (region 2, Figure 1a) first comes to the interface valleys (region 3) while the depleted solution (originating from region 1) passes over the interface hills, thus diminishing the perturbation amplitude.

In summary, a theoretical and numerical analysis that includes perturbations of the hydrodynamic flow field in addition to the solute field above the perturbed vicinal interface has been carried out. It is found that the hydrodynamic perturbations are important only at low wave numbers. Ignoring the flow perturbation, we have found an analytic condition for stability. This condition predicts absolute (not relative, as in reference [15]) stability with respect to step bunching if the shear rate S is sufficiently large. The critical shear rate depends on both capillarity and kinetics.

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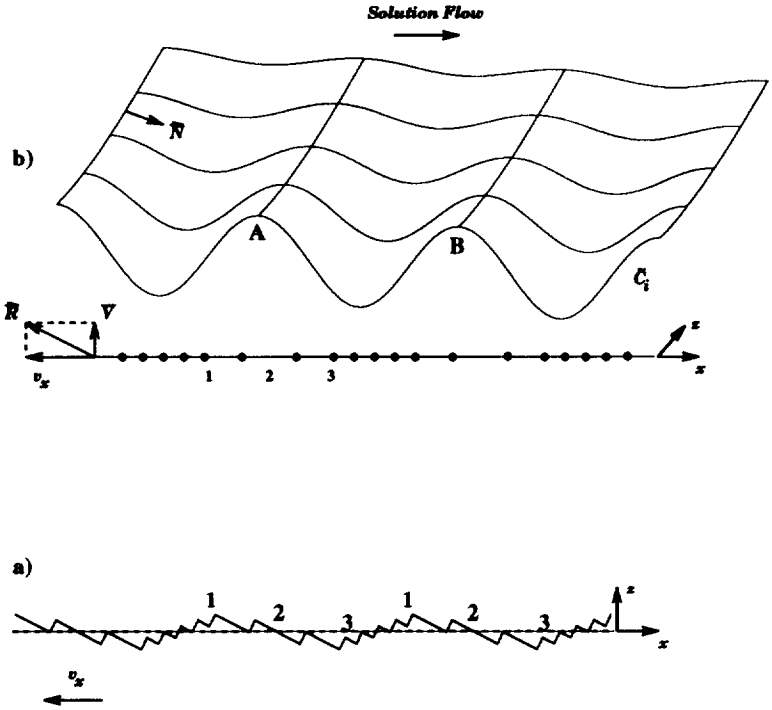

Figure 1: a) Profile of a periodically perturbed vicinal face with steps moving to the left at phase velocity v_x. The numbers indicate regions with different step densities. b) Surface plot of the perturbed concentration field. The solid circles show the relative location of the step train with respect to the concentration wave.

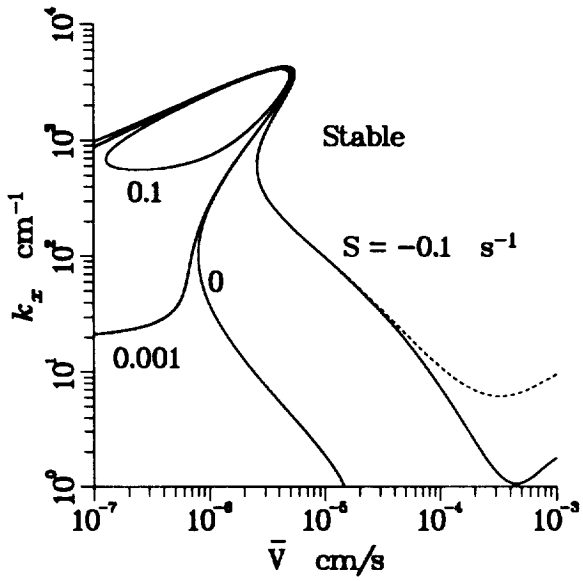

Figure 2: The spatial wavenumbers at which the system is neutrally stable as a function of growth velocity calculated numerically for $\bar{p} = 0.01$ and shear rates of -0.1, 0.0, 0.001, and 0.1 for the linear Couette profile. The solid curves are numerical solutions of the complete linear stability equations while the dashed curves neglect the perturbed flow field.